

## POROUS POLYDENDRIMERS

### CROSS REFERENCE TO RELATED U.S PATENT APPLICATIONS

This patent application relates to U.S. provisional patent application  
5 Serial No. 60/523,141 filed on November 19, 2003 entitled PERIODIC  
MESOPOROUS DENDRIMERSILICAS, and U.S. provisional patent  
application Serial No. 60/614,056 filed on September 30, 2004 entitled  
PERIODIC MESOPOROUS DENDRIMERSILICAS AND DENDRIMER  
10 INVERTED OPALS, which are both incorporated herein in their entirety by  
reference.

### FIELD OF THE INVENTION

The present invention relates to new materials, porous polydendrimers,  
and more particularly the present invention relates to periodic mesoporous  
15 polydendrimers and periodic macroporous polydendrimers, based on  
interconnected dendrimers fashioned into a structure with a periodic  
arrangement of pores at the mesoporous and macroporous length scales,  
respectively.

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### BACKGROUND OF THE INVENTION

Ordered hierarchical structures comprised of organic and inorganic  
building blocks self-assembled into architectures with dimensions spanning  
multiple length scales, akin to those in Nature's biological systems, are  
beginning to play a key role in the development of nanotechnology, see  
25 Hamley, I. W. Nanotechnology with soft materials. *Angew. Chem. Int. Ed.* 42,  
1692-1712 (2003), and Soler-Illia Galo, J de A, Sanchez C, Lebeau B.,  
Patarin J. *Chem. Rev.* 102, 4093-4138 (2002). In this context, dendrimers are  
a unique class of nanomaterials having a hyperbranched monodispersed  
30 polymer structure and an overall architecture that is well-defined in terms of  
physical size and shape, internal porosity and surface properties, enabling  
utility as chemical sensors, drug delivery systems, imaging and contrast

agents, see Newkome, G. R., He, E., Moorefield, C. N. Suprasupermolecules with novel properties: Metallocendrimers. *Chem. Rev.* 99, 1689-1746 (1999), and Fischer, M., Vögtle, F. Dendrimers: Design to Application-A Progress Report. *Angew. Chem. Int. Ed.* 38, 884-905 (1999).

5 Materials fashioned into a structure with a periodic arrangement of mesopores, e.g. MCM 41, or macropores represent a special class of compounds that portend applications in catalysis, separation science, chemical sensing and photonics, see Kresge, C. T., Leonowicz, M., Vartuli, J. C., Beck, J. C. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* 359, 710-712 (1992); Blanco, Alvaro; 10 Chomski, Emmanuel; Grabtchak, Serguei; Ibisate, Marta; John, Sajeev; Leonardo, Stephen W.; Lopez, Cefe; Meseguer, Francisco; Miguez, Hernan; Mondia, Jessica P.; Ozin, Geoffrey A.; Toader, Ovidiu; Van Driel, Henry M. Large-scale synthesis of a silicon photonic crystal with a complete 3-dimensional bandgap near 1.5 micrometres. *Nature (London)* (2000), 15 405(6785), 437-440.

20 In view of the unique properties of each of these classes of materials, it would be very advantageous to provide a method that allows the integration of these two classes of materials to create a totally new class of nanostructured organic/inorganic hybrid materials. In other words, to combine dendrimer building units with the mesoporous or macroporous structures achieved through templated assembly. The unusual combination of inorganic and 25 organic chemical structure with this scale of porosity and surfaces would permit such new materials to be used in a myriad of different applications, such as the controlled release and uptake of chemicals and drugs, chiral separations and catalysis, electronic printing, microelectronic packaging and photonic applications. These applications target the synergistic relationship between the dendrimer and the meso- or macroporous structure within a single hierarchical, nanostructured organic/inorganic hybrid material.

## SUMMARY OF THE INVENTION

The present invention provides a template directed self-assembly strategy to create nanostructured porous inorganic-organic hybrid materials we call periodic mesoporous dendrisilicas (PMeDs) and periodic macroporous dendrisilicas (PMaDs). The general class of these materials can be called periodic porous polydendrimers (PPPs), of which periodic porous dendrisilicas (PPDs) are a preferred embodiment. The unusual combination of inorganic silica and organic dendrimer chemical structures with these scales of porosity and surfaces suggests a myriad of uses for PMeDs and PMaDs, such as the controlled release and uptake of chemicals, chiral separations and catalysis, electronic printing and microelectronic packaging, biomaterial platforms, chromatography stationary phase, and photonic crystal applications. These applications target the synergistic relationship between the dendrimer and the meso- or macroporous structure within a single hierarchical nanostructured organic/inorganic hybrid material.

The present invention provides a new material comprising a porous polydendrimer with uniform pores of tunable size. The material may be in powder form, formed as a film or fiber, or as a monolith.

The porous polydendrimer may be a periodic mesoporous polydendrimer. It may also be either a macroporous polydendrimer. In a preferred embodiment the polydendrimer is a dendrisilica.

The dendrisilica may be made from any one or combination of dendrimers. In preferred embodiments the dendrisilica is made from  $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{OEt})_3]_4$  (1), or from  $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{O}-\text{i-Pr})_3]_4$  (i-Pr = isopropoxy) (2), or from  $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}((\text{C}_2\text{H}_4)\text{Si}(\text{OEt})_3)_3]_4$  (3), or from the dendrimer  $[(\text{EtO})_3\text{Si}(\text{C}_2\text{H}_4)]_3\text{SiCH}_2\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{OEt})_3]_3$  (4), or combinations thereof.

The present invention also provides a method of synthesizing a porous polydendrimer with uniform pores of tunable size, comprising:

30 mixing a dendrimer with a template under conditions suitable for self-assembly of the dendrimer to form a polydendrimer encapsulating the template; and

removing the template from the polydendrimer to give a porous

polydendrimer with uniform pores of tunable size.

The polydendrimer may be made by polymerization of a dendrimer comprising a polymerizable group at an outmost shell of the dendrimer, and wherein the polydendrimer self-assembles upon prior to polymerization of the polymerizable group.

The polydendrimer may be made by polymerization of a mixture of two or more types of dendrimers, each dendrimer of the mixture of two or more dendrimers comprising a polymerizable group at an outmost shell of each dendrimer.

The template may be selected to tune the size of the pores which remain after removal of the template, and may be molecular, ionic, non-ionic, polymers, copolymers, block copolymers, or combinations thereof, to give some non-limiting examples. In addition, the authors anticipate that a combination of mesoscale and macroscale templates may be used in combination or sequentially, to create a mesoporous/macroporous hierarchical porous polydendrimer structure.

The dendrimer may be chosen to give a polydendrimer which is a periodic macroporous dendrisilica. For example, the dendrimer may be  $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{OEt})_3]_4$  (1), or it may be  $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{O}-\text{i-Pr})_3]_4$  (i-Pr = isopropoxy) (2), or it may be  $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}((\text{C}_2\text{H}_4)\text{Si}(\text{OEt})_3)_3]_4$  (3), or it may be  $[(\text{EtO})_3\text{Si}(\text{C}_2\text{H}_4)]_3\text{SiCH}_2\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{OEt})_3]_3$  (4).

The present invention also provides a method of producing a macroporous polydendrimer inverted opal, comprising the steps of:

infiltrating a dendrimer into void spaces of a colloidal crystal template comprising colloidal particles;

polymerizing the dendrimer to form a polydendrimer; and

removing the colloidal crystal template to give a macroporous polydendrimer with uniform pores of tunable size.

The present invention also provides a method of synthesizing a periodic mesoporous macroporous polydendrimer comprising infiltrating a dendrimer and a mesoscale template into a macroscale colloidal template material under conditions suitable for polymerization of the dendrimer followed

by removing both the mesoscale and macroscale template materials from the polydendrimer/template composite to give a periodic mesoporous macroporous polydendrimer (PMeMaP).

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### BRIEF DESCRIPTION OF THE DRAWINGS

The method of producing new porous polydendrimers in accordance with the present invention will now be described, by way of example only, reference being made to the accompanying drawings, in which:

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Figure 1a shows self-assembly of 1 with ODTMABR= octadecyltrimethylammoniumbromide, the periodic mesostructured product is illustrated on the right side of the figure and its channel walls consists of a three-dimensional dendrisilica network symbolized by a modified Machatschki symbol of the dendritic repeating unit (in brackets);

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Figure 1b shows a schematic illustration of the self-assembly of a dendrimer with a polymerizable group (in this case:  $\text{Si}(\text{OEt})_3$ ) into a periodic mesoporous dendrisilica (PMeD) whereupon the  $\text{Si}(\text{OEt})_3$  groups of the dendrimer hydrolyze and then polymerize around a template, after which the template is removed to give the PMeD;

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Figure 2a) shows powder x-ray diffraction pattern and b) shows TEM images of the powder form of the surfactant-extracted PMeD-1; c) shows a  $^{29}\text{Si}$  MAS NMR spectrum and d) shows  $^{13}\text{C}$  CP MAS NMR spectrum of the surfactant-extracted PMeD-1;

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Figure 3a) shows an SEM image of an as-synthesized PMeD-1 film, b) shows a PXRD spectrum of the same film.

Figure 4 shows nitrogen adsorption data for the powder form of the surfactant-extracted PMeD, the diagram shows the type IV  $\text{N}_2$  isotherm with its BJH analysis of the mesopores (inset);

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Figure 5a) shows a low magnification SEM image of the periodic macroporous dendrisilica (PMaD), and b) shows a corresponding high magnification image; and

Figure 6 shows PXRD and TEM of the PMeD-2 (Fig. 6a-b) and PMeD-3 (Fig. 6c-d).

## DETAILED DESCRIPTION OF THE INVENTION

As used herein, the term "dendrimer" means a hyperbranched monodispersed molecule or macromolecule.

5 As used herein, the term "template" means ionic and non-ionic molecules or polymers or monodispersed colloidal particles that have a structure directing function for another molecule or polymer.

As used herein, the term "molecular template" means ionic and non-ionic molecules or polymers that have a structure directing function for another molecule or polymer.

10 As used herein, the term "colloidal crystal template" means a template consisting of monodispersed colloidal particles that exceed about 50 nm in diameter.

15 As used herein, the term "periodic mesoporous" means having an ordered arrangement of pores in terms of translational symmetry with a pore diameter between about 2 and about 50 nm.

As used herein, the term "periodic macroporous" means having an ordered arrangement of pores in terms of translational symmetry with a pore diameter greater than 50 nm.

20 As used herein, the term "polydendrimer" means a polymeric material that is composed of dendrimers that are connected by covalent bonds.

As used herein, the term "dendrisilica" means a polymer that contains building units of dendrimers linked by Si-O-Si bridges at the outmost shell of the dendrimer.

25 As used herein the term "dendrimer inverted opal" means dendrimers fashioned into a structure with periodic macropores.

As used herein, the term "surfactant mesostructure" means an ordered supramolecular assembly of surfactant molecule micelles, with a translational symmetry between about 2 and about 50 nm.

30 As used herein, the term "tunable" means being capable of being defined or pre-selected through choice of template.

The present invention describes new nanostructured organic/inorganic hybrid materials, referred to as porous polydendrimers with pores of pre-

selected, tunable size which may or may not be periodic. The porous polydendrimers may be mesoporous polydendrimers or macroporous polydendrimers.

More particularly, the present invention describes new nanostructured 5 organic/inorganic hybrid materials, referred to as periodic mesoporous dendrisilica (PMed) and periodic macroporous dendrisilica (PMaD), based on dendrimers fashioned into a structure with a periodic arrangement of mesopores or macropores, thereby integrating the classes dendrimers and periodic meso- and macroporous materials. These materials are the preferred 10 embodiment of a general class of periodic mesoporous and macroporous polydendrimers, or periodic porous polydendrimers (PPPs). The size, the uniformity and the periodicity of the pores can be tuned by the choice of template in the directed self-assembly process.

The present invention describes a method to polymerize a dendrimer 15 carrying polymerizable groups at the outermost shell in the presence of a template to give an ordered nanocomposite comprised of the template and the polydendrimer. The method of synthesizing a periodic mesoporous polydendrimer includes mixing a dendrimer with a molecular template material under conditions suitable for self-assembly and polymerization of the 20 dendrimer followed by removing the template material from the self-assembled polydendrimer to give a periodic mesoporous polydendrimer (PMeP).

The method of synthesizing a periodic macroporous polydendrimer includes infiltrating a dendrimer into a colloidal template material under 25 conditions suitable for polymerization of the dendrimer followed by removing the template material from the polydendrimer/template composite to give a periodic macroporous polydendrimer (PMaP).

In a preferred embodiment the present invention describes new 30 nanostructured organic/inorganic hybrid materials, referred to as periodic mesoporous dendrisilicas (PMedS) and periodic macroporous dendrisilicas (PMaDs), based on dendrimers fashioned into a structure with a periodic arrangement of mesopores or macropores, thereby integrating dendrimers

with periodic meso- and macroporous structure.

The present invention describes a method to polymerize a dendrimer carrying alkoxysilane groups at the outermost shell in the presence of a template to give an ordered nanocomposite comprised of the template and the dendrisilica.

The invention also describes template removal to maintain the periodic meso- or macrostructure comprised of dendrimer building blocks. Template removal can be achieved by methods such as thermal decomposition, thermolysis, solvent extraction, supercritical fluid extraction, photolytic decomposition, and plasma etching.

The present invention will be exemplified using known dendrimers (1) and (2) and novel dendrimers tetrakis[2-(tris-(triethoxy, 2-ethylsilyl)silyl)ethyl]silane having a formula  $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}((\text{C}_2\text{H}_4)\text{Si}(\text{OEt})_3)_3]_4$  (3) and bis-[tris-(2-(triethoxysilyl)ethyl)disila]methane having a formula  $[(\text{EtO})_3\text{Si}(\text{C}_2\text{H}_4))_3]\text{SiCH}_2\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{OEt})_3]_3$  (4) discussed hereinafter which all use tri-ethoxysilyl groups, however the present invention is not restricted to these as other polymerizable groups may be used in the outermost shell besides those containing silicon.

The silsesquioxane  $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{OEt})_3]_4$  (1) (Figure 1) was chosen as the precursor for PMeDs and PMaDs in the studies disclosed herein. It can be seen as the first generation of a dendrimer with the central Si atom as the core and the  $\text{Si}(\text{OEt})_3$  groups as the shell bridged to the core by  $\text{C}_2\text{H}_4$  arms. It can be synthesized from tetravinylsilane and trichlorosilane in THF with dihydrogenhexachloroplatinate as catalyst to give  $\text{Si}[(\text{C}_2\text{H}_4)\text{SiCl}_3]_4$ , which can then be converted into compound 1 utilizing ethanol, see Michalczyk, M. J., Simonsick, , W. J. Jr., Sharp, K. G. Characterization of polyfunctional alkoxysilanes using potassium (K<sup>+</sup>) ionization of desorbed species mass spectrometry. *J. Organomet. Chem.* 521, 261-266 (1996).

The inventors have demonstrated that compound 1 can be co-assembled with a surfactant mesophase in an aqueous solution to create the first periodic mesoporous dendrisilica (PMeD-1). Both powder and oriented film morphologies have been made (using compound 2), and cast monoliths

can be expected to form by the application of similar procedures. Also, it has been demonstrated that compound 1 can be infiltrated into a latex colloidal crystal template to create the first periodic macroporous dendrisilica (PMaD). Moreover, the inventors have also shown that the respective second 5 generation dendrimer  $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}((\text{C}_2\text{H}_4)\text{Si}(\text{OEt})_3)_3]_4$  (3) and a first generation dendrimer with a modified core  $[(\text{EtO})_3\text{Si}(\text{C}_2\text{H}_4)]_3\text{SiCH}_2\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{OEt}_3)]_3$  (4) can be self-assembled in a similar way to give PMeD-2 and PMeD-3.

The invention will now be described using the following non-limiting examples of dendrimers, namely compounds  $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{OEt})_3]_4$  (1), Figure 1, 10 and (2)  $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{O}-\text{i-Pr})_3]_4$  (i-Pr = isopropoxy) templated using a non-limiting example of a template, namely octadecyltrimethylammoniumbromide (ODTMABR), into a periodic mesoporous dendrisilica structure. Moreover the dendrimers 3 and 4 will be self-assembled into PMeD-2 and PMeD-3 using the non-ionic surfactant Pluronic 123™.

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## EXAMPLE 1

### Synthesis of 1 and 2

The synthesis of compound 1 was performed according to literature as 20 disclosed in Michalczyk, M. J., Simonsick, , W. J. Jr., Sharp, K. G. Characterization of polyfunctional alkoxy silanes using potassium ( $\text{K}^+$ ) ionization of desorbed species mass spectrometry. *J. Organomet. Chem.* 521, 261-266 (1996).

Compound 2 was prepared analogously, however isopropanol was 25 used instead of ethanol.

### Synthesis of Periodic Mesoporous Dendrisilica (PMeD-1)

Referring to Figures 1a and 1b, Octadecyltrimethylammoniumbromide (ODTMABR) (0.72 mmol, 270 mg, Aldrich) was dissolved in a solution of dry 30 NaOH (3 mmol, 240 mg) and 24 g de-ionized water at 20 °C. Compound 1 (2.4 mmol, 1.9 g) was added to this solution, which was stirred for 1 d at 20 °C while a white precipitate formed which is the polymerized dendrimer/template

composite. Afterwards the precipitate was aged 2 d at 80 °C which improves the periodicity of the composite. Then the precipitate was filtered off and washed with copious amounts of water. The as-synthesized sample was then stirred for 12 h in a solution of 12 g HCl (36 wt%) and 80 g of methanol to 5 remove the OCTMABR template. The sample was then filtered off again and washed with copious amounts of MeOH, to give the surfactant extracted PMeD as a powder. In Figure 1a, the final structure is shown at the right hand side which shows a hexagonally ordered PMeD with a one-dimensional pore system and the interconnected dendrimer building blocks composing the pore 10 walls. The three-dimensional dendrisilica network is symbolized by a modified Machatschki symbol of the dendritic repeating unit (in brackets) with the numeral 3 indicating a 3-dimensional structure and the fact that it is a polymer is indicated by the infinity symbol.

With particular reference to Figure 1b, there is shown a schematic 15 illustration of the above described self-assembly of a dendrimer with a polymerizable group (in this case: Si(OEt)<sub>3</sub>) into a periodic mesoporous dendrisilica (PMeD). The Si(OEt)<sub>3</sub> groups of the dendrimer hydrolyze and then polymerize around a template. After the template removal the PMeD is obtained.

20 Alternatively, instead of a powder, monoliths are made by sol-gel methods known to those skilled in the art. The dendrimers are mixed with a template in an aqueous solution to give a homogeneous sol. After gelation of the sol in the reaction vessel the PMeD is obtained as a monolith, and the template can be extracted with organic or inorganic solvents. The shape of 25 the reaction container can be used to define the shape of the monolith, see Attard, G. S., Glyde, J. C., & Goltner, C. G. (1995). Liquid-crystalline phases as templates for the synthesis of mesoporous silica. *Nature*, 378(6555), 366-368.

30 Films are made by spin-coating, dip-coating or casting a synthesis solution. A typical synthesis involves mixing 0.7125 g of 10<sup>-3</sup>M HCl, 2.2517 g EtOH, and 0.900 g aqueous cetyltrimethylammonium chloride solution (25 wt.%, Aldrich) to make a homogeneous solution, then adding 1.0457 g of

compound **2** and stirring vigorously for 30 minutes (final molar ratio 1.0 : 70.8 :  $6.54 \times 10^{-4}$  : 45.3 : 0.65 of **2** : H<sub>2</sub>O : HCl : EtOH : cetyltrimethylammonium chloride). After spin-coating at rates of 1200 – 3600 rpm onto glass or a Si (100) wafer the films were dried in air at room temperature for 24 h and 5 washed in DI H<sub>2</sub>O before calcination at 300°C under flowing nitrogen for 5 h, heating at 1 °C/min. The authors believe that a vapour deposition method may be applied alternatively.

Alternatively fibers are made by extruding or spinning a viscous sol containing the dendrimers, the template and the solvent to produce a 10 polydendrimer/template nanocomposite fiber. The template is removed from the fibers by known solvent extraction methods to leave a mesoporous polydendrimer, see Bruinsma, P. J., Kim, A. Y., Liu, J., & Baskaran, S. (1997). Mesoporous Silica Synthesized by Solvent Evaporation: Spun Fibers and Spray-Dried Hollow Spheres. *Chem. Mater.*, 9, 2507-2512.

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### Characterization of Periodic Mesoporous Dendrisilica (PMeD-1)

Figure 2a shows the powder x-ray pattern of the surfactant-extracted PMeD-1. The 100 reflection gives a d-spacing of 4.0 nm. Transmission electron microscopy (TEM) images of the PMeD provided additional structural 20 information, showing the presence of periodic arrays of parallel-aligned mesoscale channels with a spacing of 3.9 nm, mesopores of about 2.5 nm and a wall thickness of 2.3 nm (Figure 2b).

The magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy of the PMeD showed that no significant Si-C bond cleavage occurred during the synthesis. To expand on this key point, the surfactant-extracted material (Figure 2c) shows four peaks at 3.5, 53.8, 61.9 and 71.2 ppm similar to the chemical shifts for the <sup>29</sup>Si MAS NMR signals of the precursor **1**. The signal at 3.5 ppm can be assigned to the SiC<sub>4</sub> building units of the dendrimer core, while the other signals represent T<sub>1</sub> SiC(OSi)(OH)<sub>2</sub> (53.8 ppm), T<sub>2</sub> SiC(OSi)<sub>2</sub>(OH) (61.9 ppm) and T<sub>3</sub> SiC(OSi)<sub>3</sub> (71.2 ppm) 25 tetrahedral units. The cross polarization (CP) MAS NMR spectroscopy of the PMeD indicates that full removal of the surfactant had occurred by showing a 30

peak at  $-0.9$  ppm, typical for a  $\text{CH}_2\text{CH}_2$  bridge between two Si atoms.<sup>7</sup> A small signal at  $42.8$  ppm indicates some methoxylation of the silanol groups during the extraction process. By comparison all periodic mesoporous organosilicas (PMOs) to date only show T  $\text{SiO}_3\text{C}$ <sup>8</sup> or D  $\text{SiO}_2\text{C}_2$ <sup>9</sup> building blocks in their MAS NMR spectra, while the  $\text{SiC}_4$  units in PMeDs are unprecedented.

Thermogravimetry analysis of the extracted PMeD-1 performed in air or  $\text{N}_2$  revealed no significant mass loss up to  $250$   $^{\circ}\text{C}$  except the loss of some physisorbed water between  $20$  and  $100$   $^{\circ}\text{C}$ . The mesostructure of the PMeD remains with no significant pore shrinkage or decrease of order up to  $400$   $^{\circ}\text{C}$ . Above  $400$   $^{\circ}\text{C}$  pore shrinking and gradual loss of order occurs, however the mesostructure can be seen still clearly at  $900$   $^{\circ}\text{C}$ .  $^{29}\text{Si}$  MAS NMR spectroscopy of thermally treated samples under  $\text{N}_2$  showed only signals at  $3.8$  ppm for the  $\text{SiC}_4$  unit and between  $-45$  and  $-75$  ppm for the  $\text{SiO}_3\text{C}$  units up to  $400$   $^{\circ}\text{C}$ . From  $500$   $^{\circ}\text{C}$  the signals for the  $\text{SiC}_4$  units disappear almost completely while signals for Q sites ( $\text{SiO}_4$ ) appear around  $-110$  ppm.

The PMeD-1 was also obtained as a supported oriented film by spin coating onto a glass slide a mixture of  $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{O}-\text{i-Pr})_3]_4$  (2), HCl (10-3 M), cetyltrimethylammoniumchloride (CTMACl) and ethanol, which had been stirred for 20 minutes at room temperature. These films have been characterized by scanning electron microscopy SEM and powder x-ray diffraction PXRD (Figure 3a-b). In order to ensure the organic groups remained intact inside the channel walls after spin coating, 50 thin film samples were prepared on glass substrates (with area  $2 \times 2$  cm). The films were scratched off the substrate and powdered to give a 25 mg sample, which was then investigated by  $^{29}\text{Si}$  MAS NMR. These samples showed only the signal for  $\text{SiC}_4$  and  $\text{SiO}_3\text{C}$  units, thereby confirming the Si-C bonds were not cleaved in the self-assembly synthesis and film forming process.

Nitrogen adsorption data for the powder form of the PMeD-1 shows a diagnostic type IV isotherm with well-defined capillary condensation and very little hysteresis (Figure 4). The Brunauer Emmett Teller (BET) surface area is found to be as high as  $1102$   $\text{m}^2/\text{g}$  and the mesopore diameter is about  $2.5$

nm, calculated by BJH methods (Figure 4) close to that seen in TEM images (Figure 2b). This adsorption data together with the d spacing of 4.0 nm given by PXRD provides an independent estimate of the channel wall thickness of about 1.5 nm thereby corroborating the diameter of the mesopores and 5 thickness of the channel walls obtained by TEM imaging. Density functional theory (DFT) analysis of the low pressure arm of the isotherm also suggests the presence of micropores with diameters in the range of 1.0-1.5 nm, however further work is necessary to confirm this unambiguously.

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## EXAMPLE 2

### Synthesis of Periodic Macroporous Dendrisilica (PMaD)

An ordered colloidal crystal of polystyrene (PS) latex colloidal crystals of diameter ca. 200 nm was prepared by sedimentation from a stabilized 15 suspension. A solution of 0.908 g of **1** was stirred into a homogeneous mixed solution of with 0.361 g of HCl ( $10^{-3}$  M) and 0.560 g EtOH until homogeneous due to the hydrolysis of the ethoxy groups of the dendrimer, and was then dropped onto the latex colloidal crystal and allowed to infiltrate the colloidal crystal in order to polymerize the dendrimer building blocks around the 20 particles of the colloidal crystal template. The infiltrated colloidal crystal was dried at 60°C, before heating to 400°C in air for 5 hours (heating at 1°C/min) to burn away the polymer template. The colloidal crystal may be a photonic colloidal crystal characterized by intense Bragg diffraction so that the resulting structures after inversion is also a photonic crystal.

25 PMaD structures may be made using compounds **(2)**, **(3)** and **(4)** disclosed herein in addition to any other dendrimer compound. The periodic macroporous dendrisilica may be useful as photonic crystals in various optical applications, or in catalytic or biomedical applications.

### 30 Characterization of Periodic Macroporous Dendrisilica (PMaD)

The PMaD was characterized by scanning electron microscopy (SEM). The SEM images (Figures 5a and b) clearly show the periodic macroporous

structure of the PMaD, with pores of diameter ca. 200 nm.

### EXAMPLE 3

5 **Synthesis of tetrakis[2-(trivinylsilyl)ethyl]silane**

1.02 g (1.5 mmol) tetrakis[2-(trichlorosilyl)ethyl]silane were dissolved in 50 ml THF dried over Na/benzophenone. This solution was added dropwise to 27 ml of a 1 N solution of vinylmagnesiumbromide in THF (Aldrich) at room temperature within 1 h. The mixture was stirred for 24 h at room temperature and then added to 200 ml of an aqueous 1 N ammonium chloride solution mixed with ice. This mixture was shaken for 2 min until ethene evolution ceased. 200 ml of hexane were added and the mixture was transferred to a separation funnel. Then the mixture was shaken vigorously for another minute and after phase separation was completed the organic layer was separated from the aqueous layer. After removal of the hexane, a yellow oil was obtained. This raw product was further purified by column chromatography using hexamethyldisilazane treated silica gel giving pure tetrakis[2-(trivinylsilyl)ethyl]silane in a yield of 70 %.  $^{13}\text{C}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  134.65 (s,  $\text{CH}_2$ ), 134.51 (s,  $\text{CH}$ ), 4.85 (s,  $\text{CH}_2$ ), 2.61 ( $\text{CH}_2$ ).  $^1\text{H}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.1-6.3 (24H, m), 5.7-5.9 (12H, m), 0.54-0.65 (16 H, m).

20 **Synthesis of tetrakis[2-(tris-(triethoxy, 2-ethylsilyl)silyl)ethyl]silane (3)**

0.57 g (1 mmol) tetrakis[2-(trivinylsilyl)ethyl]silane, 4.7 g (18.8 mmol) trichlorosilane (Aldrich) and 3.1 ml dry THF are mixed under  $\text{N}_2$  atmosphere. To this solution 0.1 mg dihydrogenhexachloroplatinate dissolved in 0.1 ml absolute ethanol was added. The mixture was stirred for 5 h at room temperature under  $\text{N}_2$  atmosphere. To this solution 250 ml dry heptane (Aldrich) were added. Then the excess trichlorosilane and the THF was evaporated in vacuum to give a heptane solution of tetrakis[2-(tris-(trichloro, 2-ethylsilyl)silyl)ethyl]silane. To this heavily stirred solution a solution of 4.9 g (36 mmol) absolute ethanol in 250 ml heptane was added dropwise within 10 h via a dropping funnel at a pressure of 200 Torr and room temperature. The

solution was stirred for another 12 h at room temperature, then the heptane and the excess of ethanol was evaporated in vacuum to give **2** in 95 % yield.

<sup>13</sup>C (300 MHz, CDCl<sub>3</sub>): δ 58.24 (s, CH<sub>2</sub>), 18.33 (s, CH<sub>3</sub>), 3.12 (CH<sub>2</sub>), 2.76 (CH<sub>2</sub>), 2.48 (s, CH<sub>2</sub>), 1.75 (CH<sub>2</sub>). <sup>1</sup>H (300 MHz, CDCl<sub>3</sub>): δ 3.80 (72H, q), 1.22 (108 H, t), 0.2-0.65 (64 H, m). MS (ES) (m/z) = 2571 (m +23, 100 %).

### Synthesis of PMeD-2

NaCl (31.7 mmol, 1.85 g) and 0.336 g Pluronic 123 (BASF) were dissolved in 2 N HCl (8.4 g) and H<sub>2</sub>O (155 mmol, 2.8 g). To this solution bis-[tris-(2-(triethoxysilyl)ethyl)disila]methane (**3**) (0.25 mmol, 0.94 g) was added under vigorous stirring at room temperature. The mixture was stirred at room temperature for 24 h while a white precipitate formed and kept under static conditions for another 48 h at 80 °C. After filtration the PMeD was obtained as a white powder. The extraction to remove the Pluronic 123 template was carried out by stirring the as-synthesized PMeDs in a mixture of 250 ml acetone and 10 ml 2N HCl for 4 d at 50 °C. After the extraction the product was filtered off and washed with acetone and the final product is a powder.

## EXAMPLE 4

### Synthesis of bis-(trivinyldisila)methane

1 g (2.9 mmol) bis-(triethoxy)disilamethane (Gelest) were dissolved in 50 ml THF dried over Na/benzophenone. This solution was added dropwise to 27 ml of a 1 N solution of vinylmagnesiumbromide in THF (Aldrich) at room temperature within 1 h. The mixture was stirred for 24 h at room temperature and then added to 200 ml of an aqueous 1 N ammonium chloride solution mixed with ice. This mixture was shaken for 2 min until ethene evolution ceased. 200 ml hexane were added and the mixture was transferred to a separation funnel. Then the mixture was shaken vigorously for another minute and after phase separation was completed the organic layer was separated from the aqueous layer. After removal of the hexane a yellow oil was obtained. This raw product was further purified by column chromatography

using hexamethyldisilazane treated silica gel giving pure tetrakis[2-(trivinylsilyl)ethyl]silane in a yield of 70 %.  $^{13}\text{C}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  136.40 (s,  $\text{CH}_2$ ), 133.94 (s,  $\text{CH}$ ), -4.25 ( $\text{CH}_2$ ).  $^1\text{H}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.0-6.4 (12H, m), 5.7-5.9 (6H, m), 0.21 (2 H, m).

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#### Synthesis of bis-[tris-(2-(triethoxysilyl)ethyl)disila]methane (4)

1.25 g (5.3 mmol) bis-(trivinyldisila)methane, 6.4 g (47.7 mmol) trichlorosilane (Aldrich) and 5.2 ml dry THF are mixed under  $\text{N}_2$  atmosphere. To this solution 0.1 mg dihydrogenhexachloroplatinate dissolved in 0.1 ml absolute ethanol was added. The mixture was stirred for 5 h at room 10 temperature under  $\text{N}_2$  atmosphere. To this solution 250 ml dry heptane (Aldrich) were added. Then the excess trichlorosilane and the THF was evaporated in vacuum to give a heptane solution of bis-[tris-(2-(trichlorosilyl)ethyl)disila]methane. To this heavily stirred solution a solution of 15 13.1 g (286 mmol) absolute ethanol in 250 ml heptane was added dropwise within 10 h via a dropping funnel at a pressure of 200 Torr and room temperature. The solution was stirred for another 12 h at room temperature, then the heptane and the excess of ethanol was evaporated in vacuum to give bis-[tris-(2-(triethoxysilyl)ethyl)disila]methane in 95 % yield.  $^{13}\text{C}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  58.31 (s,  $\text{CH}_2$ ), 18.25 (s,  $\text{CH}_3$ ), 3.25 (s,  $\text{CH}_2$ ), 2.25 ( $\text{CH}_2$ ).  $^1\text{H}$  (300 20 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.80 (36H, q), 1.20 (54 H, t), 0.40 - 0.65 (24 H, m), -0.33 (2 H, s). MS (ES) ( $m/z$ ) = 1239 (m +23, 100 %).

#### Synthesis of PMeD-3

25 NaCl (31.7 mmol, 1.85 g) and 0.336 g Pluronic 123 (BASF) were dissolved in 2 N HCl (8.4 g) and  $\text{H}_2\text{O}$  (155 mmol, 2.8 g). To this solution bis-[tris-(2-(triethoxysilyl)ethyl)disila]methane (4) (0.66 mmol, 0.94 g) was added under vigorous stirring at room temperature. The mixture was stirred at room temperature for 24 h while a white precipitate formed and kept under static 30 conditions for another 48 h at 80 °C. After filtration the PMeD was obtained as a white powder. The extraction of the Pluronic 123 template was carried out by stirring the as-synthesized PMeDs in a mixture of 250 ml acetone and 10

ml 2N HCl for 4 d at 50 °C. After the extraction the product was filtered off and washed with acetone again to give a powder product.

### Characterization of PMeD-2 and PMeD-3

5 The PXRD and the TEM of the PMeD-2 and PMeD-3 (Figure 6) show that also these materials can be reproducibly made with a high degree of mesostructural order with the PXRD providing a d-spacing of 14.4 nm (PMeD-2) and 14.1 nm (PMeD-3). Furthermore TEM suggests pore sizes of about 8 nm and a pore wall thickness of ca. 6 nm.  $^{29}\text{Si}$  MAS NMR investigations  
10 showed two signals for the  $\text{SiC}_4$  (11 ppm) and  $\text{SiO}_3\text{C}$  (59 ppm) building units for PMeD-2 (10 and 58 ppm for PMeD-3). The integration of the signals revealed a molar ratio of 1 : 3.1, which is slightly higher than the theoretical value of 1 : 2.4, indicating that some of the  $\text{SiC}_4$  units have transformed into  $\text{SiO}_3\text{C}$  units, most likely originating from some minor Si-C bond cleavage.  
15 However, the NMR data suggests that the majority of the dendrimer building units keep intact during self-assembly. Similar the integrals for PMeD-3 showed a ratio of 1 : 4.1 instead of 1 : 3. It is noteworthy that no  $\text{SiO}_4$  units are observed in the material. The integral ratios were reproducible with varying pulse delay times between 3 and 30 s indicating that the  $^{29}\text{Si}$  nuclei are  
20 sufficiently relaxed to give accurate integrals. Nitrogen isotherms demonstrated the ordered mesoporous nature of both PMeD-2 and PMeD-3 by showing typical type IV isotherms. The Brunauer-Emmett-Teller surface area was found to be 775 (PMeD-2) and 767  $\text{m}^2 \text{ g}^{-1}$  (PMeD-3). The BJH analysis revealed a narrow pore size distribution with average pore sizes of  
25 9.1 (PMeD-2) and 8.2 nm (PMeD-3), which is consistent with the TEM data.

### Instrumentation

PXRD patterns were measured with a Siemens D5000 diffractometer using  $\text{Cu K}\alpha_1$ -radiation ( $\lambda = 154.18 \text{ pm}$ ). TEM images were recorded on a Philips 430 microscope at an accelerating voltage of 200 kV (film fragments on C film-coated Cu grids). All solid state NMR experiments were performed with a Bruker DSX 400 NMR spectrometer.  $^{29}\text{Si}$  MAS-NMR spectra were recorded at a spin rate of 5 kHz and a pulse delay of 5 s.  $^{13}\text{C}$  CP MAS-NMR

experiments were performed at a spin rate of 5 kHz, a contact time of 5 ms and a pulse delay of 3 s. TGA experiments were carried out with a Perkin-Elmer TGA7 instrument with a heating rate of 1 °C. Sorption experiments were performed by a Quantachrome Autosorb-1C machine with N<sub>2</sub> as sorption gas at 77 K starting at a relative pressure p/p<sub>0</sub> = 10-5. 7 data points were selected for BET analysis from relative pressure of 0.1. SEM images were recorded with a Hitachi S-4500 microscope at 1 kV (no Au coating).

With the work presented herein the inventors have demonstrated for the first time that a dendrimer shaped molecule can be fashioned into a periodic meso- or macroporous structure to create a new class of nanostructured organic/inorganic hybrid that we call periodic mesoporous dendrisilicas (PMeDs) and periodic macroporous dendrisilicas (PMaDs). The general class of these materials are referred to herein as porous polydendrimers, of which periodic porous polydendrimers (PPPs) are preferred, and more preferred are porous dendrisilicas (PPDs). The inventors contemplate that other organic, inorganic or organic-inorganic dendrimers with different cores, arms and generations can also be self-assembled by similar structure-directed template-based synthetic methods to form new families of PMeDs and PMaDs in which the properties of dendrimers are synergetically combined with those of periodic meso- and macroporous materials. Various other templates such as different ionic surfactants, block copolymers or colloidal crystals of other length scales can be expected to be useful templates to tailor the pore size. Because the template defines the size and uniformity of the pores, the pore size is said to be tunable. The template also defines the periodic structural phase (ie; 2D hexagonal, FCC), but also can include non-periodic structures having uniform pore size distribution (ie; worm-like mesoporous structures). The variety of choice for the dendrimer and template makes these materials important and useful for a broad range of applications. Non-limiting examples of applications are low-k materials for microelectronics, separation technologies, e.g. chiral drug separations or waste water cleaning, catalysis, drug delivery, chemical storage, e.g. gas storage, and sensors including biosensors. The use of larger scale colloidal

crystal templates makes these dendritic macroporous materials suitable for photonic applications or as a scaffold for biomedical tissue growth, in combination with the applications mentioned above.

It will be appreciated that compounds **1**, **2**, **3** and **4** are non-limiting examples only and that the core may be one of numerous elements or organic or inorganic groups not restricted to silicon, the number of shells may be varied and may involve combinations of organic/inorganic, pure organic etc. The dendrimer has to carry a polymerizable group at the outmost shell which in the present example is achieved using tri-alkoxysilyl groups in the outmost shell. However, it will be appreciated by those skilled in the art that other polymerizable groups may be used which are not restricted to tri-alkoxysilyl groups. For example, vinyl groups or trichloro-silyl groups may be used, just to give non-limiting examples.

It will be appreciated that different template materials may be used, with the choice of template material being selected to give for example selective control of pore size in the mesoporous or macroporous structure. While surfactants in general may be used, it will be understood that colloidal crystal templates may be used, or combinations thereof. It will also be appreciated that a periodic mesoporous macroporous polydendrimer (PMeMaP) may be synthesized by infiltrating a dendrimer and a mesoscale template into a macroscale colloidal template material under conditions suitable for polymerization of the dendrimer followed by removing both the mesoscale and macroscale template materials from the polydendrimer/template composite.

The properties of the resulting mesoporous or macroporous polydendrimer depend on the nature of the core, the arms and the number of generations, template and structure type, e.g. MCM41, MCM48 etc. Basic areas of application are microelectronics (low k materials), separation techniques (e.g. chiral drug separation), bio-delivery, chemical storage (e.g. gas storage), catalysis.

Post-synthesis steps may include adding various reactive groups on the dendritic building block, the use of the porous polydendrimer as a

template and inversion of the porous polydendrimer.

As used herein, the terms "comprises" and "comprising" are to be construed as being inclusive and open ended, and not exclusive. Specifically, when used in this specification including claims, the terms "comprises" and "comprising" and variations thereof mean the specified features, steps or components are included. These terms are not to be interpreted to exclude the presence of other features, steps or components.

The foregoing description of the preferred embodiments of the invention has been presented to illustrate the principles of the invention and not to limit the invention to the particular embodiment illustrated. It is intended that the scope of the invention be defined by all of the embodiments encompassed within the following claims and their equivalents.

## References

1. Hamley, I. W. Nanotechnology with soft materials. *Angew. Chem. Int. Ed.* 42, 1692-1712 (2003).
2. Soler-Illia Galo, J de A A, Sanchez C, Lebeau B., Patarin J. *Chem. Rev.* 102, 4093-4138 (2002).
3. Newkome, G. R., He, E., Moorefield, C. N. Suprasupermolecules with novel properties: Metallocendrimers. *Chem. Rev.* 99, 1689-1746 (1999).
4. Fischer, M., Vögtle, F. Dendrimers: Design to Application-A Progress Report. *Angew. Chem. Int. Ed.* 38, 884-905 (1999).
5. Kresge, C. T., Leonowicz, M., Vartuli, J. C., Beck, J. C. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* 359, 710-712 (1992).
6. Michalczyk, M. J., Simonsick, , W. J. Jr., Sharp, K. G. Characterization of polyfunctional alkoxy silanes using potassium (K<sup>+</sup>) ionization of desorbed species mass spectrometry. *J. Organomet. Chem.* 521, 261-266 (1996).
7. Inagaki, S., Guan, S., Fukushima, Y., Ohsuna, T., Terasaki, O. Novel Mesoporous Materials with a Uniform Distribution of Organic Groups and Inorganic Oxide in Their Frameworks. *J. Am. Chem. Soc.* 121, 9611 (1999).
8. Asefa, T., Ozin, G. A., Grondy H., Kruk, M., Jaroniec, M. Recent developments in the synthesis and chemistry of periodic mesoporous organosilicas. *Stud. Surf. Sci. Catal.* 141, 1 (2002).
9. Landskron, K., Hatton, B. D., Perovic, D. D., Ozin, G. A. Periodic mesoporous organosilicas containing interconnected [Si(CH<sub>2</sub>)]<sub>3</sub> rings. *Science* 302, 266 (2003).
10. Bruinsma, P. J., Kim, A. Y., Liu, J., & Baskaran, S. Mesoporous Silica Synthesized by Solvent Evaporation: Spun Fibers and Spray-Dried Hollow Spheres. *Chem. Mater.*, 9, 2507-2512 (1997).
11. Attard, G. S., Glyde, J. C., & Goltner, C. G. Liquid-crystalline phases as

templates for the synthesis of mesoporous silica. *Nature*, 378(6555), 366-368 (1995).